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TRANSFORMER HEADSPACE SAMPLING AND ANALYSIS FOR THE PRESENCE OF POLYCHLORINATED BIPHENYLS

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SUMMARY

Given the chemical and physical stability of polychlorinated biphenyls (PCBs), it has been of increasing concern to regulators to monitor and screen samples of various types for PCB contamination. In particular, proposed changes to EU regulations may require all UK Distribution Network Operators (DNOs) to determine if their transformers are contaminated with PCBs. This study investigated the feasibility of sampling the air in the headspace of a transformer through the breather pipe to determine the presence of PCBs using the standard method for measuring PCBs in air. It was found that PCBs were only detectable when the test transformer was heated, and, even then, they were present in the headspace at very low levels (pptv). This leads to the conclusion that headspace measurements are not suitable for detecting PCBs in live, pole-mounted transformers.

1 INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of man-made, aromatic Persistent Organic Pollutant (POP) compounds which were introduced worldwide in the late 1920’s (1). Given the chemical and physical stability of polychlorinated biphenyls (PCBs), it has been of increasing concern to regulators to monitor and screen samples of various types for PCB contamination. In particular, proposed changes to EU regulations may require all UK Distribution Network Operators (DNOs) to determine if their transformers are contaminated with PCBs. PCBs are semi-volatile compounds where congeners with a lower degree of chlorination are more volatile than those with a higher degree. When they volatilise, they form vapours which are heavier than air.

A review of the current and potential techniques to determine the level of PCB contamination in transformer oil was carried out in WP1.1 of this project and a cost benefit analysis was carried out in WP1.2. This report describes the work carried out in WP1.3 – Transformer Headspace Analysis.

Western Power Distribution (WPD) are looking to find a method of determining the presence of PCBs in the transformer oil used in their transformers both on the ground and pole mounted. Ideally, they want to be able to do this without taking the transformers offline because of the substantial costs involved in doing this. Sampling the oil via the breather pipe has been ruled out at this stage as it may lead to debris falling into the oil and contaminating it which may, in turn, lead to a failure in the insulation properties of the oil. Drilling or piercing the oil reservoir has also been ruled out because of the risk of swarf causing the same issue.

The method investigated here involves sampling the air above the oil reservoir to detect the presence of PCBs in the vapour phase. This is as a feasibility investigation to understand if PCBs are present in this phase to understand if it is possible to use the methods identified in WP1.1 that can measure low levels of PCBs in air.

2 BACKGROUND

2.1 OBJECTIVE

The aim of this work package is to determine if PCBs are present in the headspace of a transformer containing contaminated oil, at levels detectable using the EPA method TO-10A (2). This method requires 24 hours of sampling and is therefore not an appropriate method for testing a large number of transformers for PCB contamination. However, it will show whether sampling the headspace of a transformer is a feasible option via other, more expensive and sensitive techniques, and so whether further work to develop online headspace sampling is worthwhile. If this is possible, the need to both isolate the transformer from the network or contaminate the oil during sampling may be avoided.

2.2 ESTIMATES OF HEADSPACE PCB CONCENTRATION

From knowledge of the vapour pressure of the lightest PCB congeners, an estimate of the amount *n* (mol) of PCBs in the headspace can be made using the ideal gas law.

$$n = \frac{PV}{RT}$$

Where, P = vapour pressure (Pa), V = headspace volume (m^3), R = Gas Constant = 8.314 m^3.Pa/K.mol and T = temperature K.

Table 2.1: Lightest PCB congener properties at 25 °C in 1m^3 (5).

PCB Congener	Formula	Vapour Pressure (Pa)	Concentration (mol/mol)	Molecular Mass (g/mol)	Mass / g
Monochlorobiphenyl	$C_{12}H_9Cl$	1.1	2.21992E-06	188.5	0.000418
Dichlorobiphenyl	$C_{12}H_8Cl_2$	0.24	4.84345E-07	223	0.000108
Trichlorobiphenyl	$C_{12}H_7Cl_3$	0.054	1.08978E-07	257.5	2.81E-05
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	0.012	2.42173E-08	292	7.07E-06
Pentachlorobiphenyl	$C_{12}H_5Cl_5$	2.60E-03	5.24707E-09	326.5	1.71E-06

The values in Table 2.1 represent pure PCBs at a temperature of 25°C (3). If the total concentration of PCBs in a volume of transformer oil was 50 parts per million (ppmv) for these congeners, then for a sampling period of 24 hours and a flow rate of 10 l/min, the total mass of PCBs (first 5 congeners) in the headspace would be 0.1 µg. This assumes the vapour pressure is maintained as the air is sampled. However, the mixture of congeners in transformer oil varies and therefore is not known for a given transformer. It is likely that the concentration of these lighter congeners would be much less as a proportion of the total concentration. The estimated value of 0.1 µg suggests that at this temperature and pressure, detecting the presence of PCBs in the headspace of a transformer is challenging.

The higher the temperature of contaminated oil, the higher the vapour pressure of the PCBs in it. The plot of vapour pressure vs temperature shown in Figure 2.1 suggests that vapour pressure increases by about a factor of 3 or 4 from 25°C to 40°C (4). Therefore, heating the transformer oil will increase the concentration of PCBs in the headspace.

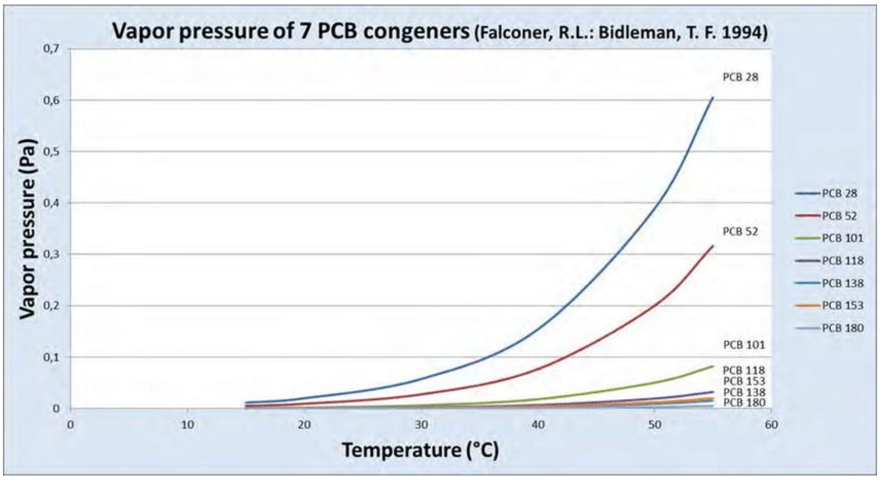

Figure 2.1: Vapour pressure of the 7 most PCBs most likely to be hazardous to health in environmental applications with respect to temperature (4).

3 MATERIALS & METHODS

3.1 EQUIPMENT

3.1.1 Sampling media

The standard method involves actively sampling the air in the headspace of the transformer through the use of sorbent tubes consisting of Tenax sandwiched between two layers of polyurethane foam (PUF) (SKC 226-124), at 5 l/min for 24 hrs. These tubes have a limit of detection (LoD) of 1 µg using GCMS-ECD analysis. Estimates of the PCB concentration that might be expected in a transformer would suggest that this LoD is not low enough. An alternative sorbent tube, SKC 226-129 (Figure 3.1), was identified which was designed to meet EPA and ASTM method specifications for high flow sampling of PCBs in ambient air. This tube consists of XAD$^{®}$-2 sorbent sandwiched between the two PUF layers. This tube combined with High-Resolution Gas Chromatography Mass Spectrometry (HR-GCMS) analysis, has an LoD of 0.5 ng - 1 ng which would provide a better chance of detecting PCBs in the headspace. The SKC 226-129 tubes were therefore chosen as the most suitable sampling media for this feasibility study. Though these tubes are high flow tubes and are normally used with flows of around 200 l/min, this flow is not practical for this experiment and lower flows were used. This is not expected to have any impact on the capture efficiency of the tubes. The air was sampled from the breather pipe outlet of the transformer.

Figure 3.1: SKC 226-129

3.1.2 Pumps

Two vacuum pumps, a Leybold Trivac D4B and a Becker DT/VT 4.4, were used to carry out the sampling as per EPA method TO-10A. The Becker pump was used to simultaneously sample the background while the Leybold Trivac sampled the transformer headspace.

3.1.3 Experimental Setup

A sampling media holder was designed, and 3D printed for the purpose of this experiment as suitable holders are not readily commercially available for this application, see Figure 2.3.

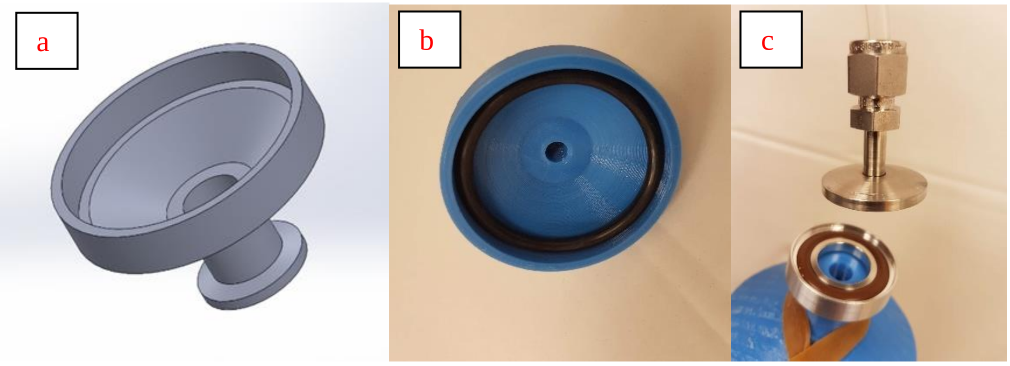

Figure 2.3: SKC 226-129 sampling holder – a) 3D design, b) 3D printed holder with O-ring, and c) connections from holder to sampling tubing.

The SKC 226-129 tubes were held in place using the 3D printed holders, connecting them to the vacuum pump on one end and the breather tube of a test transformer via tubing on the other. This allowed the sampled headspace air to pass through the sampling tube at a flow controlled by the pump. The test transformer was supplied by WPD which had a known contamination of ~50 ppm total PCBs. The experimental set up deployed at the WPD site in Exeter is shown in Figure 2.4.

Figure 2.4: Experimental setup using a test transformer with ~50 ppm PCB contamination.

3.2 EXPERIMENTAL

3.2.1 Headspace Sampling

Two methods to extract the air from the headspace of the test transformer were performed. The first involved sampling the air close to the end of the breather tube outlet. This had the advantage that it was easy to position the sampling media and a reasonable air flow through it was maintained. The proportion of air from the headspace compared to the surrounding air, however, was expected to be low.

The second method attempted to seal the end of the breather tube so that only air from the headspace was sampled. This had the advantage that most of the air sampled was from the headspace. A perfect seal was not expected nor were the seals around the transformer lid airtight, therefore, air from the surroundings was also extracted.

Both methods 1 and 2 were repeated, however, this time while attempting to heat the oil in the transformer above room temperature. WPD supplied an industrial infrared heat lamp to do this which was positioned approximately 50 cm away from the test transformer for the sampling period. Due to time and equipment constraints, the oil did not reach a steady, controlled temperature. The temperature was recorded at the start and at the end of sampling using a laser thermometer.

3.2.2 Test Plan

Five tests were carried out using the SKC 226-129 tubes. The first test was a background measurement where the air in the room housing the test transformer was actively sampled for 24 hours at approximately 37 l/min. This gave an understanding of the background levels of PCBs present in the room housing the transformer. The second and third tests involved sampling from the breather tube of both the test oil at room temperature and the test oil heated using method 1 mentioned above. The fourth and fifth tests involved sampling from the breather tube of both the test oil at room temperature and the test oil heated using method 2. Table 3.1 summarises the tests that were carried out.

Table 3.1: Summary of the 5 tests carried out on the test transformer at Exeter.

Test	Sampling time	Temperature (°C)	Flow Rate (l/min)
Background	24 hours	16	37
Unsealed	24 hours	16	41
Unsealed and heated	24 hours	Between 20 and 60	41
Sealed	24 hours	16	-
Sealed and heated	24 hours	Between 20 and 60	-

3.2.3 Flow Measurements

Prior to the transformer tests in Exeter, the air flow through the sampling tube was measured using a Mesalabs DryCal 1020 mass flow meter. This meter is capable of measuring flows between 5 – 500 sL/min with a measurement uncertainty of ± 0.25% of the reading, 95% confidence interval. The sampling tube and both pumps were connected to the DryCal 1020 so that air was drawn through it before flowing through the tube and then the pump.

The pump used for the background sampling was measured to have an average of 37.34 sL/min over 11 measurements with a standard deviation of 0.06 sL/min. The average was taken once the readings had stabilised, in this case after 5 measurements. The vacuum pump took slightly longer to stabilise, reaching a stable reading after 16 measurements. The average flow measured over 15 measurements was 41.02 ± 0.07 sL/min. The average flow measured with the ballast switched on was 41.63 ± 0.07 sL/min and without the tube was 41.48 ± 0.05 sL/min.

It was not possible to measure the flow rate through the filter for the sealed case as the flow meter was not available at the test site at the time of testing.

3.2.4 Analyses

Following the sampling of the contaminated transformer, the samples were sent off to Marchwood Scientific Services, a UKAS accredited laboratory, for analyses using HR-GCMS. The analysis was carried out according to EPA method TO-10A for the EC-7. The EC-7 refers to the standard suite of PCBs designated by the EU as those congeners that are most likely to be hazardous to health in environmental applications. Marchwood Scientific Services was the only UKAS accredited laboratory found to analyse PCBs in air samples in the UK.

4 RESULTS & DISCUSSION

A summary of the results from Marchwood Scientific is shown in Table 4.1. Information on each congener can be found in Table 1a in the appendix section of this report. Table 4.2 shows the concentration of the background and unsealed tests in parts per trillion by volume (pptv) calculated taking the sampling time and flow rate into account. The flow could not be recorded during the sealed tests, however, given that the values in Table 4.1 are comparable to the background values, the sealed tests appear to give insignificant results.

Table 4.1: Results of the EC-7 concentrations in ng / sample for each of the five sampling tests.

Test	PCB-28	PCB-52	PCB-101	PCB-153	PCB-138	PCB-180
Background	15	29.8	28.1	7.1	5.85	0.748
Sealed	12.7	15.7	8.87	5.61	2.93	3.33
Unsealed	16.6	34	27.8	10.9	6.36	4.14
Unsealed & heated	48.6	158	664	1262	953	1066
Sealed & heated	9.72	17.2	13.8	10.7	5.46	5.81

Table 4.2: Results of the EC-7 concentrations in ppt for each of the five sampling tests.

Test	PCB-28	PCB-52	PCB-101	PCB-153	PCB-138	PCB-180
Background	0.282	0.559	0.527	0.133	0.110	0.014
Unsealed & heated	0.823	2.676	11.247	21.375	16.142	18.056
Unsealed	0.281	0.576	0.471	0.185	0.108	0.070

From plotting the results from Table 4.2, it is clear that PCBs have only been detected above background during the unsealed & heated test with PCB-153 being the largest component (Figure 4.1). However, if we compare the results from the other four tests in ng/sample, we can see that the three lightest PCBs are the dominant congeners in the vapour phase in background air and transformer headspace (Figure 4.2). This indicates that the ratio of the different cogeners is different for the heated headspace when compared to background air samples. This shows that all PCBs must be heated to be detectable in the vapour phase above background, in particular, the heavier PCBs in the vapour phase increase upon heating.

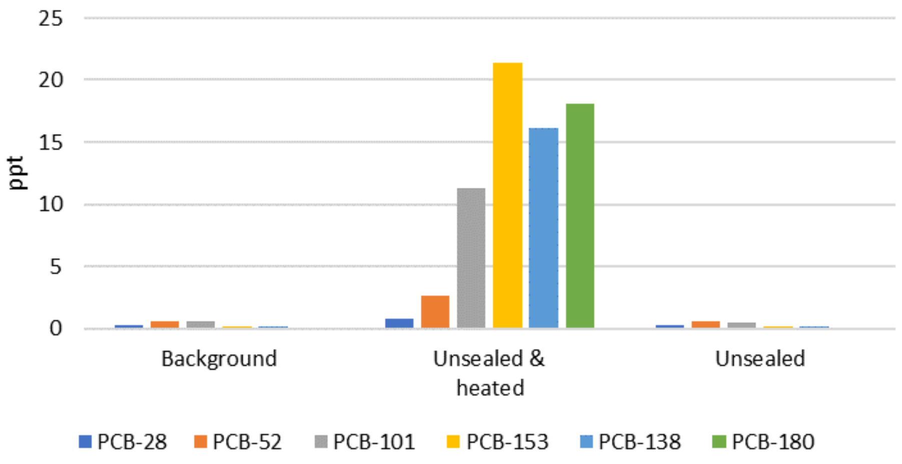

Figure 4.1: Comparison of the background, unsealed & heated, and unsealed results in pptv.

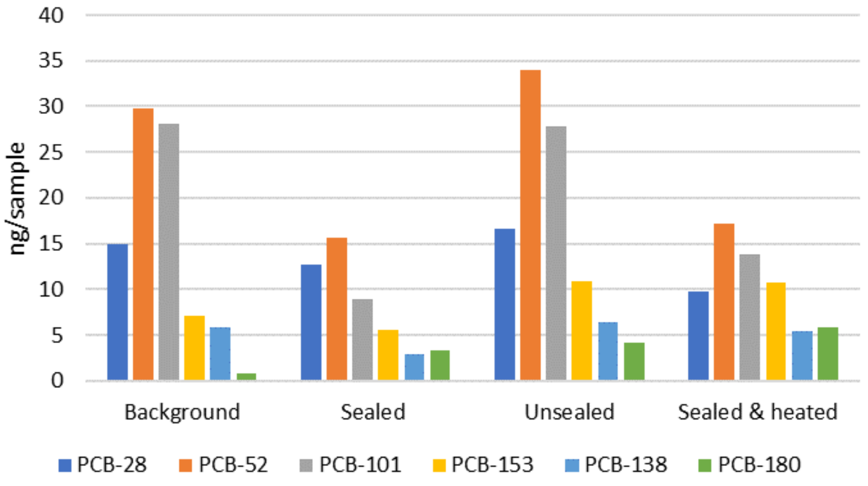

Figure 4.2: Comparison of the results excluding the unsealed & heated in ng/sample.

Given these results, it can be concluded that the transformer oil must be heated to approximately 60°C in order for PCBs in the vapour phase to measure above background using this method. However, even with heating, it would appear that a contaminated transformer with a concentration of approximately 50 ppm, contains 22 pptv or less PCBs in the vapour phase. The technique identified in WP1.1, PTR-TOF-MS, has claimed to have the ability to detect PCBs in the vapour phase as low as 4 pptv, however, thus far this has only been investigated in a laboratory setting. Furthermore, to deploy this method in the field, it would require coupling with either special heated inlet hoses or live-line rods for sampling the air from the transformer headspace. Again, as stated in WP1.1, if PTR-TOF-MS is chosen as the technique to take forward for this application, further testing will be required to understand the partition function of different PCB congeners and a correlation curve will need to be generated using different concentrations of PCBs in different oil samples. This correlation between the levels of PCBs in the gas phase to the concentration of PCBs in the oil is required in order to provide discrimination near to the 50 ppm limit value, to avoid either too many false positives or false negatives.

5 CONCLUSIONS

This feasibility study has shown that PCBs are not present at detectable levels in the headspace of transformers unless the oil in the transformer is heated. Even if the transformer is approximately at a temperature between 20°C and 60°C, PCBs may only be present in the low ppt levels, with the transformer containing at least 50 ppm of PCBs overall. The technique identified in WP1.1, PTR-TOF-MS may have the ability to measure PCBs at this ppt level, however, this instrument has yet to be used to sample, detect and quantify PCBs in practice and has only shown its ability to measure standard PCB mixes in a laboratory setting. Given that this technique is very expensive for one instrument, further research to investigate the use of this instrument for this application is necessary. If this is not possible, one option for a cost-effective method that currently exists for identifying transformers that are contaminated with a concentration of > 50 ppm of PCBs, is the integrated oil sampling system consisting of specialized live line tools, sampling siphon and vial, sealing rivet and paint method offered by the Canadian company, Powertech Labs Inc. Powertech claim this can be used on energised transformers and reliably seals the transformer after safe sampling. We have not, however, had the opportunity to explore the practical and validated use of this system.

6 REFERENCES

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APPENDIX

Table 1a: List of EC-7 PCBs in order of size. All information was found on the following website: https://pubchem.ncbi.nlm.nih.gov

Congener	IUPAC Name	Molecular formula	Molecular Weight (g/mol)
PCB-28	2,4,4'-Trichlorobiphenyl	$C_{12}H_7Cl_3$	257.5
PCB-52	2,2',5,5'-Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	292
PCB-101	2,2',4,5,5'-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	326.4
PCB-153	2,2',4,4',5,5'-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	357.8
PCB-138	2,2',3,4,4',5'-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	360.9
PCB-180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	$C_{12}H_3Cl_7$	395.3